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Discussions

Interactive comment on "Linking the lithogenic, atmospheric, and biogenic cycles of silicate, carbonate, and organic carbon in the ocean" *by* S. V. Smith and J.-P. Gattuso

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Dr. Ridgwell begins "*The authors, to some credit, have refused to blindly accept established theories about the long-term regulation of atmospheric* pCO_2 *via (silicate) rock weathering (the "silicate weathering thermostat"), and present a paper questioning the accepted theory*". This is an extravagant statement, as nowhere in the manuscript is the role of silicate weathering in the long-term regulation of atmospheric pCO_2 questioned.

Ridgwell also claims that we are really focusing on (calcium) silicate weathering and implies that we do so because it is easier to deal with $CaCO_3$ reactions. This may be what he would have preferred us to focus on, but the claim is baseless. This misrepresentation is repeated elsewhere in his report. As we state, the focus of this paper is on a problem we first recognized many years ago with respect to calcium carbonate reactions in seawater, not on calcium silicate or other silicates. We focused on $CaCO_3$, and particularly seawater reactions, because that is where the problem was revealed. Indeed, Berner et al (1983) explicitly observe that an imbalance between in the 1:1 molar ratio between $CaCO_3$ precipitation and CO_2 gas release would quickly exhaust atmospheric CO_2 exactly as we observed. They then assume that such a balance must occur without examining the thermodynamics of the $CaCO_3$ reaction. To their credit, their model explicitly deals with organic carbon reactions, without noting that this would solve the problem we pose. Lerman and Mackenzie (2005) accept the existence of $\Psi < 1.0$ and build it into their model, also without explicitly explaining the phenomenon. Of course their model also includes organic carbon reactions. and where it has now been resolved. As far as we are aware, there is no comparable problem with the silicate cycle. So any suggestion that we are dealing carbonates even though we are really interested in silicates is spurious.

The specific issue that we posed is that an asymmetry between freshwater $CaCO_3$ reactions (mostly dissolution) and seawater reactions (mostly precipitation) present an asymmetry in net CO_2 flux between the hydrosphere and atmosphere. Yet eqs. 1-3 are based on symmetric flux with respect to $CaCO_3$ dissolution and precipitation. With seawater and despite eq. 2, there is not a 1:1 balance between $CaCO_3$ reactions and CO_2 flux. This can be demonstrated theoretically and experimentally. That equation is qualitatively, but not quantitatively, correct. Rather, for seawater (where most carbonate precipitation occurs), the molar CO_2:$CaCO_3$ flux ratio is about 0.6:1 (surface water) or about 0.9:1 (present water-column integrated).

Silicate reactions are conceptually important in the discussion, because silicate and carbonate dominate the global weathering and precipitation cycle. At steady state, according to theory, silicate mineral and CO_2 derived from the Earth's interior react

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to form $CaCO_3$ and SiO2 (eq. 3), with no net change of atmospheric CO_2. We have recognized an asymmetry in flux following the $CaCO_3$ reactions, but are aware of no evidence for such asymmetry in silicate reactions. Therefore the conundrum lies entirely with $CaCO_3$. Because net carbonate dissolution occurs on land while net precipitation occurs in the ocean, the classical view of the linked carbonate-silicate weathering and precipitation cycle as represented by eqs. 1-3 overestimates the CO_2 release by $CaCO_3$ precipitation. The downward correction in this flux is quantitatively significant and merits explanation.

There are not two independent cycles here: carbonate and silicate. This fact has been recognized for well over 150 years. Rather, as represented traditionally, there is one cycle that involves the weathering and precipitation of both carbonate and silicate minerals, with the steady state requirement that there be a balance in CO_2 flux to and from the atmosphere (as formalized in the Urey equations in 1952).

Moreover, the chemical reactions and their behavior in strict response to equilibrium constraints (i.e., physical chemistry) of the aqueous CO_2 system must be followed. The defining constants shift with temperature, salinity, pressure, and ionic strength, but these shifts (for the carbonate reactions, where the problem exists) have been considered in our analysis. If these are explicitly built into models (as is the case with Lerman and Mackenzie, 2005), then there is no problem –but not necessarily a capture of the mechanism. Models such as that of Berner et al. (1983) may or may not have explicitly captured the mechanism– but it may be implicit by their inclusion of organic carbon. Our point here is not to fault individual models, but rather to point out the underlying physical chemistry behind the problem and to observe that the standard equation couplet (carbonate-silicate) should really be a triplet (carbonate-silicate-organic matter).

We point out that, given the difference between CO_2 partitioning in freshwater and seawater and the consequent fluxes of CO_2 in response to $CaCO_3$ reactions, this traditional pair of equations is not quantitatively in balance. We discuss this briefly, but carefully, in the introduction and point explicitly to eq. 3 as the historically purported

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(Urey) balance between eqs. 1 and 2. To repeat, this historically purported balance is not met quantitatively because of the differing behavior of the carbonate sub-cycle in freshwater (where CO_2 flux follows the expectation of eq. 1) and seawater (where it does not). We then point out that addition of organic reactions to the pair of traditional reactions can be used to resolve this issue. This is evident in the geochemical behavior of the Hawaii water column inorganic carbon profile (Figure 1), apparently beyond where Dr. Ridgwell quit reading. Having done this, we then examine water column (one-dimensional) behavior as a CO_2 sink in response to the combination of $CaCO_3$ and organic C reactions and atmospheric CO_2 under various hypothetical, but instructive, scenarios.

The importance of organic matter in weathering processes has long been recognized. Bob Berner has both pointed out in various cited papers that the organic cycle should be part of the consideration of geochemical weathering and precipitation reactions and has pointed out the long (if qualitative) historical recognition of this point. Our contribution is the explicit observation that inclusion of organic matter reactions reconciles the quantitative anomaly that appears with respect to CO_2 release back to the atmosphere in the traditional weathering and precipitation cycle. Dr. Ridgwell has missed this point.

Dr. Ridgwell poses the following question at the end of his paragraph "*We can play a simple thought experiment...*" as follows: "*...would the authors really claim that given enough cycles of transferring CO_2 and air-sea equilibrium, that all of the CO_2 would eventually end up in the ocean and a new steady-state would be reached with no CO_2 in the atmosphere? This, is in effect, what they are proposing.*"

Yes, this is pretty much the thought experiment we are presenting, **in the absence of other factors**. We point out that something like this would occur and would do so on a time scale of $\sim 10^4$ years. Examination of the main other factor is the focus of this paper.

Berner et al. (1983), in their paper presenting the well-known BLAG model, arrived at much the same conclusion we have, with respect to rapid exhaustion of atmospheric CO_2 if there were an imbalance in the carbonate sub-cycle. Those authors expressed their version of the imbalance calculation in a slightly different manner than we did (a 10% reduction in addition of CO_2 to the atmosphere via oceanic $CaCO_3$ precipitation), so the time scale they arrived at to exhaust atmospheric CO_2 was somewhat different from ours: $\sim 3 \times 10^4$ years. Nevertheless, the point remains that the imbalance implied by Ψ would quickly exhaust atmospheric CO_2, **all other factors remaining constant**.

Similarly, Lerman and Mackenzie (2005) explicitly build the effect of Ψ into their model, although they do not arrive at an explanation for the behavior.

Having thus demonstrated the magnitude of the imbalance, we then introduce organic reactions along with $CaCO_3$ in order to resolve the issue. That is discussed in the text (apparently beyond the point where Ridgwell quit reading) and is not repeated here.

Ridgwell is miffed because we have "*omitted the climate dependency on weathering*" We have omitted it because it is irrelevant to our paper. The chemical equations must be satisfied, regardless of any dependency of rates on climate. The point is that the simple underlying equation for the $CaCO_3$ reaction does not work without an additional chemical equation. We have pointed out that organic organic matter reaction is apparently that equation. Given the fact that far more organic matter is formed and oxidized in the world ocean that the amount of $CaCO_3$ precipitated (and largely dissolved), it should come as no surprise that organic metabolism should be included as one of the three (not two) basic chemical equations describing weathering and precipitation reactions. We see no room for argument on this point.

Dr. Ridgwell observes:

> *BUT, when you remove 1 mol of CO_2 from the atmosphere in the initial weathering reaction, carbon re-partitions between ocean and atmosphere. Hence, it is not 1 mol of CO_2 that one must replenish in the atmosphere*

> *through carbonate precipitation and CO_2 release, but rather less. There is also a repartitioning of CO_2 between the ocean and atmosphere upon addition of the weathering products (Ca^{2+} + 2 HCO_3^-) to the ocean (but before precipitation). In fact, the cycle is closed, and atmospheric CO_2 is left unaltered at steady state and the atmosphere is in no danger of becoming "exhausted" of CO_2 as the authors suggest.*

The problem with this interpretation is as follows. Let us assume for simplicity that net $CaCO_3$ dissolution on land is exactly balanced by net $CaCO_3$ precipitation (and burial) in the ocean. We assign the process of carbonate dissolution a rate of X (because the dissolution process takes up CO_2 at a 1:1 molar ratio). The carbonate species redistribution in the rivers occurs, but is misleading. This is all part of the process by which the CO_2 enters the fresh water in response to the $CaCO_3$ dissolution. In the ocean, the net (water-column integrated) value for Ψ is presently about 0.9. Therefore the gas release is +0.9X.

Dr. Ridgwell's closing paragraph underscores a problem with his argument. He apparently thinks that uptake of atmospheric CO_2 by rainwater is a significant pathway by which DIC enters fresh water. This is actually not correct. As pointed out in their simple, but elegant, case studies of inorganic C geochemistry by Garrels and Christ (1965) very little atmospheric CO_2 would be taken up into freshwater without the effects of organic matter oxidation. In fact those authors close those case studies (p. 88) by observing:

> *In summary, it can be said that the role of CO_2 in rainwater probably has been overrated, whereas the effects of hydrolysis and of CO_2 in the soil atmosphere have been underrated.*

While it is true that pCO_2 (and therefore Ψ) will rise as river water mixes with seawater, the primary control on the CO_2 content and pCO_2 of the water is generally organic reactions. It seems, wherever we look, that we cannot escape the fact that organic matter reactions figure prominently in weathering and precipitation reactions. However, this is outside the boundary of what we set out to do. Our clearly stated mission was to put the peculiar existence of $\Psi < 1.0$ in the context of chemical reactions governing dissolution and precipitation of $CaCO_3$. We believe we have done that.

In summary, we do not believe that A. Ridgwell has provided a valid criticism of this paper. We wish he had carefully read and reviewed all of the paper we wrote instead reading a bit, then drifting off and inventing his own view of what he thought we intended to write –and then reviewing that invention.

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